

The coil-globule transition of confined polymers

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We study long polymer chains in a poor solvent, confined to the space between two parallel hard walls. The walls are energetically neutral and pose only a geometric constraint which changes the properties of the coil-globule (or “ θ ”) transition. We find that the θ temperature increases monotonically with the width D between the walls, in contrast to recent claims in the literature. Put in a wider context, the problem can be seen as a dimensional cross over in a tricritical point of a ϕ^4 model. We roughly verify the main scaling properties expected for such a phenomenon, but we find also somewhat unexpected very long transients before the asymptotic scaling regions are reached. In particular, instead of the expected scaling $R \sim N^{4/7}$ exactly at the (D -dependent) theta point we found that R increases less fast than $N^{1/2}$, even for extremely long chains.

I. INTRODUCTION

Thin films and quasi low dimensional systems are of obvious technological interest, in areas ranging from electronics to anti-corrosion coatings. Due to this, also critical phenomena in systems which are finite in one direction but infinite in all other ones have been studied in quite some detail [1, 2]. As the thickness of the film decreases, the properties cross over from bulk (3d) behaviour to surface (2d). Actually, in the true thermodynamic limit the system should show the scaling typical for 2d critical phenomena for all finite thicknesses. But since the behaviour must, for finite systems, resemble those of 3d critical systems when the thickness is larger than the lateral size, the amplitudes in the thermodynamic must show some special scaling. All this is known as *dimensional cross over*. The forces exerted by the critical fluctuations on the walls are known as Casimir forces [2]. The phenomenon exists also for tricritical points, although it has been studied much less for them.

Long flexible polymers in very diluted solutions can be described as the limit of the ϕ^4 $O(n)$ vector model in the limit $n \rightarrow 0$ [4]. The coil-globule (“theta”) transition happening as the solvent quality becomes worse (typically as temperature is lowered) is in this framework described as a tricritical point. Therefore, the problem of a polymer confined within the gap between two parallel plane walls is formally described as a dimensional cross over, either at a normal critical point (athermal polymers) or at a tricritical point (theta polymers), and the forces exerted by such a polymer are analogous to (critical/tricritical) Casimir forces.

But polymers have some special features which find no close analogy in $O(n)$ models with $n > 0$. One of them is the fact that the volume occupied by an athermal polymer of fixed chain length N and confined within two athermal walls with distance D does not depend monotonously on D [5]. If D is larger than the Flory radius $R_F \propto N^\nu$ (with $\nu \approx 0.5876$), then the main effect of the confining walls is to reduce the size perpendicular to the walls, and thus both the gyration and the end-to-end radius shrink with decreasing D . But when

the polymer is strongly compressed ($D \ll R_F$), then the main effect is the lateral swelling due to the increased excluded volume interaction. In this case, $R^2 = R_\perp^2 + R_\parallel^2$ and the occupied volume $R_\perp \times R_\parallel^2$ both increase when D is decreased further.

This observation was the basis for a recent claim [6] that the theta temperature T_θ of a polymer in a poor solvent between two athermal walls should also be non-monotonic in D . The argument is essentially that the monomer density controls the number of monomer-monomer contacts, and thus also T_θ : The higher is the density, the more effective will be the attractive monomer-monomer interaction, and the higher will be T_θ . Therefore, as D is increased, T_θ should start at its 2d value, increase, go through a maximum, and finally decrease in order to reach its 3d value when $D \rightarrow \infty$. This predicted behaviour was then supported by exact enumeration studies of short chains ($N \leq 20$) on the simple cubic lattice (see Fig. 6 below).

In the present paper we show by means of rather extensive Monte Carlo simulations that this is not correct, and that T_θ increases monotonically with D . This is essentially what one would have expected from a dimensional cross over of a tricritical point. On the other hand, some of the details of this cross over are somewhat surprising. In particular, we find extremely long transients. At $T = T_\theta(D)$, the asymptotic scaling $R_\parallel \sim N^{\nu_{\theta,2}}$ with $\nu_{\theta,2} = 4/7$ being the Flory exponent for 2d theta polymers [7, 8] is not seen even when $R_F/D \approx 100$, although we have no reason to doubt that it will hold for $R_F/D \rightarrow \infty$. The same is true for the free energy: Although we have no doubt that the scaling appropriate for 2d theta polymers will apply asymptotically at $T = T_\theta(D)$, it is not yet seen in the simulations.

These simulations are done with the pruned-enriched Rosenbluth method (PERM) [9] which is ideally suited for this purpose. It allows to study extremely long chains (for $D = 60$ we went up to $N = 600,000$) with very high statistics, and it gives immediately very precise estimates of free energies. Throughout the paper we shall model the polymers by self avoiding walks on the simple cubic lattice with attractive energy $-\epsilon$ between non-bonded

neighbouring monomers. Instead of quoting temperatures or values of ϵ , we shall describe thermal effects in terms of the Boltzmann factor

$$q = e^{\epsilon/k_b T} \quad (1)$$

per contact. The partition sum is therefore

$$Z_N(q, D) = \sum_m C_{N,m}(D) q^m \quad (2)$$

where $C_{N,m}(D)$ is the number of walks with N steps and m monomer-monomer contacts. The width D is defined such that $D = 1$ corresponds to the standard square lattice. For large D we used hashing as described e.g. in [10] in order to minimize storage demands.

II. NUMERICAL RESULTS

In the following, we will denote by $q_\theta(D)$ the value of the Boltzmann factor at the true quasi-2d theta point. The Boltzmann factor for 3-d theta polymers in the bulk is then $q_\theta^{(3)} = \lim_{D \rightarrow \infty} q_\theta(D)$, while the Boltzmann factor for strictly 2-d theta polymers on the square lattice is $q_\theta^{(2)} = q_\theta(D = 1)$. The same notation is used for theta temperatures and for growth constants (inverse critical fugacities). Growth constants at temperatures different from the collapse point will be denoted as $\mu(q, D)$, so that e.g. $\mu_\theta^{(3)} = \lim_{D \rightarrow \infty} \mu(q_\theta^{(3)}, D)$.

Exactly at the 3-d tricritical (theta) point, we can assume finite size scaling ansatzes for the partition sum and for the rms. end-to-end distances both parallel and perpendicular to the walls:

$$Z_N(q_\theta^{(3)}, D) \approx [\mu_\theta^{(3)}]^N \Phi(D/R_F(N)), \quad (3)$$

$$\begin{aligned} R_{N,\parallel}(q_\theta^{(3)}, D) &= \langle (x_N - x_0)^2 + (y_N - y_0)^2 \rangle \\ &\approx R_F(N) \Psi_\parallel(D/R_F(N)) \end{aligned} \quad (4)$$

and

$$R_{N,\perp}(q_\theta, D) = \langle (z_N - z_0)^2 \rangle \approx R_F(N) \Psi_\perp(D/R_F(N)), \quad (5)$$

up to logarithmic corrections [9, 10, 11, 12]. Here, $R_F(N)$ is the Flory radius (rms. end-to-end distance of chains in the bulk) which scales at the theta point like $N^{1/2}$, again up to logarithmic corrections. The scaling functions $\Phi(z)$, $\Psi_\parallel(z)$, and $\Psi_\perp(z)$ are finite and non-zero in the limit $z \rightarrow \infty$. Finally, the growth constant $\mu_\theta^{(3)}$ is a non-universal constant which for the present model is $5.0479050 \pm 0.0000005 + (q_\theta^{(3)} - 1.3087) \times 1.616$ [8, 9, 13].

If the theta temperature $T_\theta(D)$ increases with $1/D$, sufficiently long polymers at $q = q_\theta^{(3)}$ will be collapsed for finite D (i.e., $R_N(q_\theta^{(3)}, D) \sim N^{1/2}$), while they will be swollen ($R_N(q_\theta^{(3)}, D) \sim N^{3/4}$) if $T_\theta(D)$ decreases with

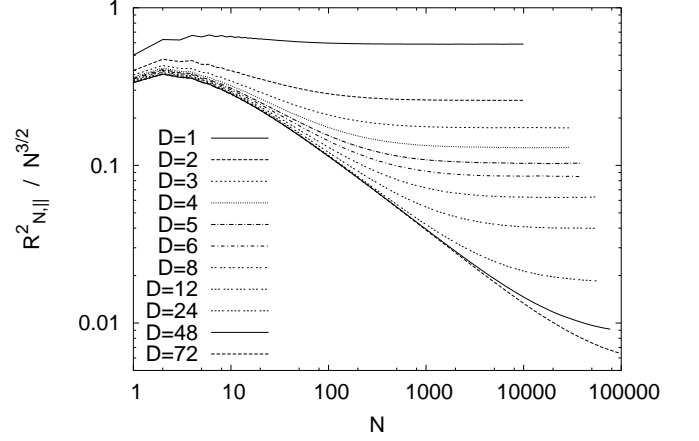


FIG. 1: Squared end-to-end distances parallel to the walls, divided by $N^{3/2}$, plotted against N . For self avoiding walks in 2d one has $R^2 \sim N^{3/2}$, i.e. the walks are swollen coils if the lines become horizontal for large N .

$1/D$. In Fig. 1 we plot $R_{N,\parallel}^2(q_\theta^{(3)}, D)/N^{3/2}$ against N , for various values of D . We see that all curves become horizontal for large N , i.e. all chains are swollen. This is in contradiction to the claim of [6]. The reason why the heuristics leading to this claim were wrong is indeed quite clear: The location of the theta point is determined by polymers whose Flory radius is much larger than D , while the anomaly noticed by van Vliet *et al.* [5] concerns only polymers with $R_F \approx D$.

From Eq.(4) we see that $\Psi_\parallel(z) \sim z^{-1/2}$ for $z \rightarrow 0$, in order to obtain $R_{N,\parallel}(q_\theta^{(3)}, D) \sim A(D)N^{3/4}$ with some amplitude $A(D)$. The D -dependence of the amplitude is then also fixed by Eq.(4),

$$A(D) \sim D^{-1/2}. \quad (6)$$

To check this, we plot in Fig. 2 the amplitudes obtained by fitting horizontal lines to the large- N data in Fig. 1. We see that the behaviour is roughly as predicted in Eq.(6), but not quite. There are obviously substantial logarithmic corrections (similarly large corrections are also seen in theta polymers in the bulk, see [9, 10, 12]). In the eyeball fit shown in Fig. 2 these are described by a factor $\propto \ln(D)^{1/4}$, but this is just done to guide the eyes. A similarly good fit would have been obtained with a pure power law $A(D) \sim D^{-0.54}$.

For all values of D , the partition sum for $N \gg D^{1/\nu_2}$ is also compatible with the scaling behaviour expected for 2-d SAWs ($\nu_2 = 3/4$ is the Flory exponent in 2 dimensions),

$$Z_N(q_\theta^{(3)}, D) \sim Z_0(D) \mu(q_\theta^{(3)}, D)^N N^{\gamma_2 - 1}, \quad (7)$$

where $\gamma_2 = 43/32 = 1.34375$ and where $-k_B T_\theta^{(3)} \ln \mu(q_\theta^{(3)}, D)$ is the free energy per monomer in the thermodynamic limit. This is compatible with

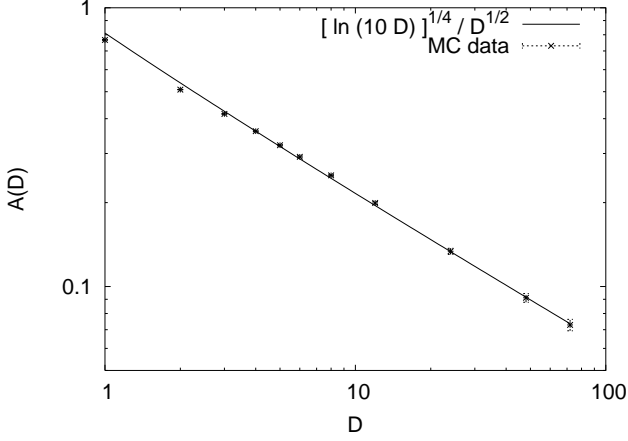


FIG. 2: Amplitudes for the end-to-end distance parallel to the walls (see Eq.(6)) plotted against D . The smooth line is an eyeball fit with a power law $\propto D^{-1/2}$ modified by a logarithmic term.

Eq.(3), provided that

$$\frac{\mu(q_\theta^{(3)}, D)}{\mu_\theta^{(3)}} \approx 1 - \frac{a}{D^2}, \quad (8)$$

$$Z_0(D) \sim D^{2-2\gamma_2}, \quad (9)$$

and

$$\Phi(z) \sim \exp(-a/z^2) \quad \text{for } z \rightarrow 0. \quad (10)$$

Eq. (8) can also be derived from field theory [1, 2, 3, 14], using De Gennes' mapping onto the $O(N=0)$ model. Numerical values for $\mu_\theta^{(3)} - \mu(q_\theta^{(3)}, D)$ are shown in Fig. 3. They are obviously in agreement with Eq. (8) for large values of D , although there are large corrections for finite D .

Up to now we have only discussed the behaviour at the theta point of the free ($D = \infty$) polymer. Let us finally study the behaviour at and in the vicinity of the theta points for the quasi-2d systems at fixed finite D . According to the above results, this corresponds, for any finite D , to temperatures where the free 3-d polymer would be collapsed. Asymptotically, for $N \rightarrow \infty$, the behaviour exactly at the tricritical point should be that for 2-d theta polymers,

$$Z_N(q_\theta(D), D) \sim [\mu(q_\theta(D), D)]^N N^{\gamma_{\theta,2}-1} \quad (11)$$

and

$$R_{N,\parallel}(q_\theta(D), D) \sim N^{\nu_{\theta,2}}. \quad (12)$$

Here, $\nu_{\theta,2} = 4/7$ and $\gamma_{\theta,2} = 8/7$ are the Flory and entropic exponents for 2-d theta polymers.

In Figs. 4 and 5 we show $R_{N,\parallel}^2(q, D)/N^{8/7}$ versus N , for several values of q close to (tri-)criticality, and for

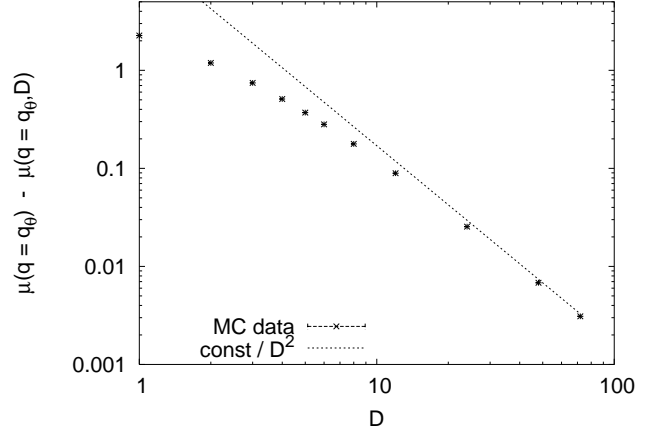


FIG. 3: Dependence of the effective connectivity constant $\mu(q, D)$ on D , for fixed $q = q_\theta^{(3)}$. The straight line gives the asymptotic behaviour $\sim 1/D^2$, which is obviously modified by logarithmic corrections. Error bars on the MC data are much smaller than the symbol sizes.

$D = 5$ (Fig. 4) resp. $D = 60$ (Fig. 5). According to Eq.(12), one of these curves in each graph should become horizontal for $N \rightarrow \infty$. Naively, one might expect this regime to set in when the (3-d) Flory radius is roughly equal to D , i.e. for $N \approx 25$ in Fig. 4 and for $N \approx 4000$ in Fig. 5. We do not see this, although our values of N are much larger than these, by factors more than one hundred. Although we cannot pin down precisely $q_\theta(D)$ due to this, we definitely see that R_N increases at the (D -dependent) theta point – and for numerically accessible values of N – slower than \sqrt{N} (straight lines in Figs. 4 and 5). Thus instead of being swollen, as predicted by theory, the polymers seem to be *collapsed* at the 3-d theta point. Similar results were found for all other values of D , and they are corroborated by the results obtained for Z_N . Also for Z_N , the asymptotic behaviour stated in Eq.(11) was not seen for any of the chains (data not shown).

While these results might look very surprising at first sight, it is indeed not too difficult to understand them heuristically. As we said, free 3-d chains would be slightly collapsed at the temperatures shown in Figs. 4 and 5. In a blob picture, these chains are therefore chains of blobs, each one of size $\approx D$, and each representing a short 3-d polymer slightly below the theta point. It is well known [9, 10, 12] that the 3-d theta collapse of finite chains happens at an effective (“Boyle”) temperature $T_\theta(N)$ which is lower than the true $T_\theta^{(3)}$, and that concatenating such chains at $T_\theta(N)$ leads to a longer chain which is much more collapsed than its short constituents: For temperatures slightly below $T_\theta^{(3)}$, there is a regime in N where $dR_N/dN < 0$, i.e. chains actually shrink when more monomers are attached to them! For the present problem this means that each blob might be swollen, but when two blobs are brought in contact, they might not repel each

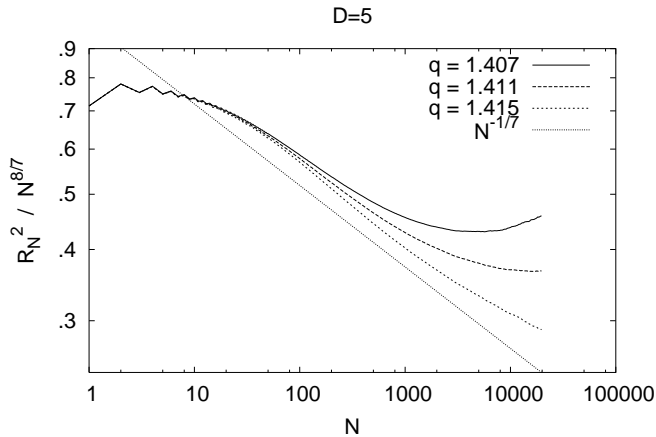


FIG. 4: Average squared end-to-end distances parallel to the walls for nearly tricritical polymers in a slit of width $D = 5$. More precisely, $R_N^2/N^{8/7}$ is plotted against $\ln N$, which would lead to a horizontal curve if Eq.(12) were satisfied for all N . The straight line indicates, in contrast, a non-swollen behaviour $R_N^2 \propto N$.

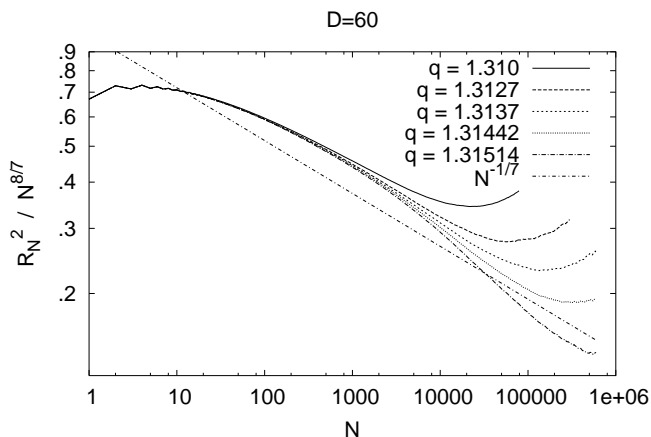


FIG. 5: Same as Fig. 4, but for $D = 60$. Notice that the longest chains in this case have $N = 600,000$.

other (as in a swollen polymer), but they rather attract each other. Obviously this is what happens. For much longer chains than those we can simulate, this would finally stop: When too many blobs are penetrating each other, repulsion finally dominates again and the chains behave as ordinary 2-d theta polymers.

According to this discussion we can give only lower bounds on $q_\theta(D)$. They are given by those values of q for which the curves in plots like Figs. 4 and 5 become horizontal. These bounds, which should however be not too far from the true values of $q_\theta(D)$, are shown in Fig. 6. We see an essentially linear increase with $1/D$. Extrapolating linearly to $1/D \rightarrow 0$ we find a value $q = 1.305 \pm 0.001$ which is close to, but definitely smaller than, $q_\theta^{(3)} = 1.3087 \pm 0.0003$ [9]. This confirms that the

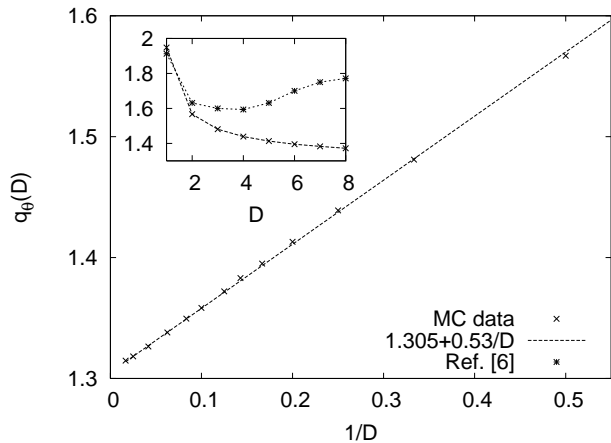


FIG. 6: Lower limit estimates of $q_\theta(D)$, plotted against $1/D$. The straight line is $q = 1.305 + 0.53/D$. The insert shows same of these data plotted against D , together with the data from Ref. [6] for comparison.

curves in Figs. 4 and 5 which become horizontal at the largest values of N are not yet the critical ones, and that the true asymptotic behaviour is not yet seen in these figures.

III. DISCUSSION

On the one hand we have shown that some recent claims about re-entrant behaviour of polymer collapse in restricted geometries are wrong. The theta collapse of a polymer confined to the space between two parallel walls is very much as expected from a tricritical behaviour in a film (quasi-2d) geometry. In particular, the collapse temperature is, for any distance D between the walls, shifted to temperatures lower than the theta temperature of free 3-d polymers, and the decrease of the free energy with decreasing D is as predicted from the theory of tricritical Casimir effects.

But on the other hand, we found that the detailed behaviour at the true quasi-2d theta collapse is – for any chain length we could simulate, and presumably also for any chain length realistic in any foreseeable experiment – rather different from the predicted one. This is related to the fact that the upper critical dimension of theta collapse (as of any other tricritical phenomenon) is $d = 3$. Therefore long chains are, at the collapse point, composed of blobs which are essentially free random walks but which slightly attract each other.

In view of the analogy between theta collapse and other tricritical phenomena, it is of interest to speculate whether similar anomalies should be expected also for the latter. For tricritical Ising or Potts models one might then expect that the effective correlation length exponent is not given by the true tricritical exponent for $d = 2$ (which is larger than $1/2$ for all these models), but

has a value $< 1/2$. To our knowledge this has neither been predicted so far, nor has it been seen in simulations or in real experiments.

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- [1] M. Krech and S. Dietrich, Phys. Rev. A **46**, 1886 (1992).
 - [2] M. Krech, *The Casimir Effect in Critical Systems* (World Scientific, Singapore 1994).
 - [3] M. Krech, J. Phys. C **11**, R391 (1999).
 - [4] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca 1979).
 - [5] J.H. van Vliet and G. Brinke, J. Chem. Phys. **93**, 1436 (1990); J.H. van Vliet, M.C. Luiken, and G. Brinke, Macromolecules **25**, 3802 (1992).
 - [6] P.K. Mishra and S. Kumar, J. Chem. Phys. **121**, 8642 (2004).
 - [7] B. Duplantier and H. Saleur, Phys. Rev. Lett. **59**, 539 (1987).
 - [8] P. Grassberger and R. Hegger, J. Phys. I France **5**, 597 (1995).
 - [9] P. Grassberger, Phys. Rev. E **56**, 3682 (1997).
 - [10] P. Grassberger and R. Hegger, J. Chem. Phys. **102**, 6681 (1995).
 - [11] B. Duplantier, J. Chem. Phys. **86**, 4233 (1987).
 - [12] J. Hager and L. Schäfer, Phys. Rev. E **60**, 2071 (1999).
 - [13] unpublished
 - [14] U. Ritschel and M. Gerwinski, Physica A **243**, 362 (1997).